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XPS and UPS study of the effect of annealing on the surface states of hydrofluoric acid treated silicon surfaces

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Abstract : Hydrofluoric acid (HF) is the standard etchant used for silicon wafers to remove the native oxide (SiO_2) from the surface. However, this process leaves behind traces of contaminants like carbon, fluorine, oxygen *etc* absorbed on the surface The present study deals with the chemical state of the HF treated silicon surface investigated by the X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron Spectroscopy (UPS) methods. XPS studies on silicon surface treated with different concentration of HF show a minimum contamination level and unpinning of Fermi level at about 5% concentration. It is found that carbon is physisorbed while fluorine and oxygen are chemisorbed as Si–F and Si–OH respectively. Further, the effect of annealing of HF treated silicon surface shows a shift in the peak position of XPS and UPS spectra towards lower binding energy upto 540°C annealing temperature. Above 540°C, again the pinning of the Fermi level occurs due to desorption of hydrogen and breaking of Si–H bonds giving rise to high density of surface states.

Keywords : Surface states, photoelectron spectroscopy, binding energy

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Extensive studies [1–4] have been done to improve the cleaning procedure in order to prepare stable surfaces and interfaces of silicon with low density of surface states and interface states suitable for device applications. Surfaces of silicon wafers are prepared with great care in clean rooms using electronic grade chemicals and high resistivity deionised (DI) water. The normal cleaning procedure leaves behind a thin layer of native oxide [5,6] which is unstable and seriously affect the electronic properties of the surface. Hydrofluoric ancid (HF) is found to be the best etchant to remove the oxides and clean the silicon surface [7,8] that is to be used in device fabrication. It is well established that HF treated silicon

*Indian Telephone Industry, Bangalore-560 016, India surface is electronically inert [9] and has a low recombination velocity [10] due to low density of surface states. This is attributed to the passivation of silicon dangling bonds at the surface by fluorine [11] and hydrogen [12]. However, this process also leaves behind certain contaminants like carbon, oxygen *etc* absorbed on the surface which may affect the growth of oxide [13–15] and the surface and interface properties of the silicon wafer. In the present investigation we have tried to identify the chemical state of the HF treated silicon surface using XPS and UPS methods. The effect of HF concentration and annealing temperature on the chemical state and electronic properties of the surface are also studied.

Polished silicon wafers of p-type and n-type <111> orientation are used in the present investigation. The wafers are cleaned in trichloroethylene, acetone and methyl alcohol to remove the organic impurities, followed by HNO_3 to remove the metallic impurities from the surface. Then the wafers are dipped in buffered HF (34.6% NH_4F, 6.8% HF and 58.6% DI water) to remove the native oxide, rinsed in DI water dried by nitrogen jet. Finally the wafers are given a controlled HF treatment by immersing for a minute in aqueous solutions of HF of varying concentrations from 2% to 48%. The HF treated wafers being hydrophobic, they are immediately transferred to the X-ray Photoelectron Spectrometer through the load-lock chamber to minimize contamination. The XPS and UPS measurements are performed using ESCALAB Mark II instrument. The details of the experiment are given elsewhere [16].

XPS results on HF treated silicon surface :

Figure 1 shows the low resolution (50 eV pass energy) XPS survey spectra for the HF treated (a) and untreated (b) silicon surface. In the untreated surface, the predominant lines

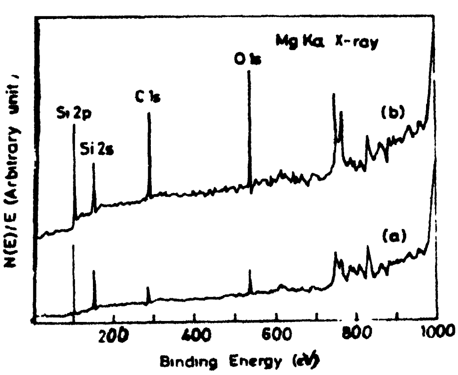

Figure 1. A representative XPS survey spectra for silicon surface at a take off angle of 55° : (a) HF (5% conc) treated surface, (b) Untreated surface.

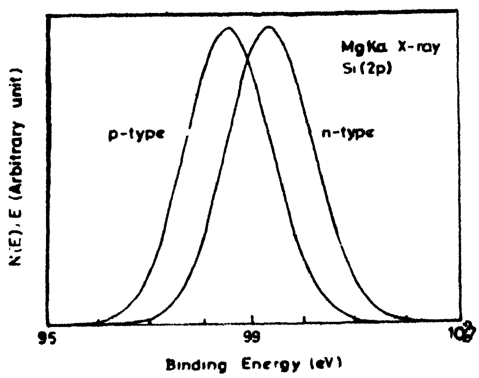

Figure 2. Si 2*p* core level photoemission spectra of HF treated n- and p-type silicon (111) surface.

are identified as O 1*s* (532.4 eV), C 1*s* (284.6 eV), Si 2*s* (150 eV) and Si 2*p* (98.7 eV). In the HF treated surface, there is a considerable reduction in the oxygen and carbon levels. The surface contamination coverage for HF treated samples are computed from the intensities of the adlayer peak and the silicon peak using the sub-monolayer theory of Carley and Robertz [17]. Table 1 gives the variation of surface contamination on the HF

Table 1. Surface coverage of contaminants on silicon surface treated with hydrofluoric acid of different concentration.

HF conc. %	Surface coverage of the contaminants (10^{13} cm^{-2}) Carbon 1*s*	Fluorine 1*s*	Oxygen 1*s*
2	10.1	3.5	4.0
3	7.5	3.7	2.6
5	4.5	4.1	2.1
7	12.5	4.8	2.5
10	16.5	5.4	2.6
20	17.6	7.8	2.7
30	18.2	9.5	2.8
48	18.6	11.5	3.0

treated surface as a function of HF concentration. It is found that around 5% HF concentration, the carbon and oxygen contaminants are minimum. From the binding energies, it is identified that oxygen and fluorine are chemically bonded to silicon in the form of Si–OH bond and Si–F bond respectively, while carbon is physisorbed in the form of hydrocarbons. The hydrocarbon contamination on the silicon surface could be due to the hydrophobic nature of the HF treated surface.

Effect of annealing on the electronic state of the silicon surface :

It is well known that presence of high density of surface states in silicon pin the Fermi level at around 0.35 eV above the valence band edge. Controlled surface treatments are required to passivate the surface and unpin the Fermi level in order to make the silicon surface suitable for device application. Figure 2 shows the XPS results on HF treated n- and p-type silicon surfaces. A separation of ~0.80 eV, observed in the binding energy of n- and p-samples, nearly corresponds to the difference in the position of the respective bulk Fermi levels. This can be attributed to the unpinning of Fermi level at the silicon surface by passivation of silicon dangling bonds by hydrogen and fluorine.

The effect of annealing temperature on XPS spectra of Si 2*p* core level of the HF treated silicon surface is shown in Figure 3. It is seen that the position of the peak shifts towards the lower binding energy as the annealing temperature increases. The magnitude of shift is small up to about 375°C, followed with a large shift between 375°C and 540°C, and above 540°C practically there is no further shift in the peak position. The total shift in the binding energy is about 0.50 eV which is nearly equal to the difference between the bulk Fermi level and the pinning position of the Fermi level at the surface. The magnitude of the shift (0.50 eV) represents the bending of the bands or the surface potential. The abrupt transition in the Si 2*p* peak position at 540°C corresponds to the desorption temperature of hydrogen [18,19] from the silicon surface. Thus above 540°C, again the pinning of the Fermi level occurs due to the breaking of Si–H bonds. This is further verified by studying

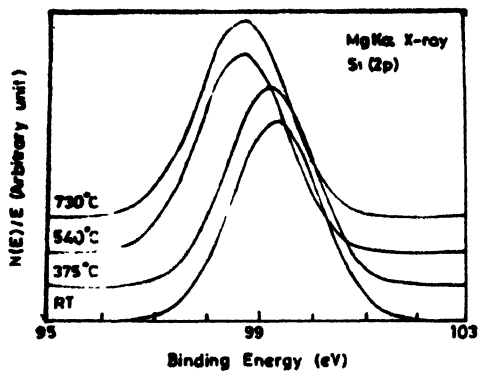

Figure 3. Si 2*p* XPS spectra of HF treated n-type silicon (111) surface at different annealing temperature.

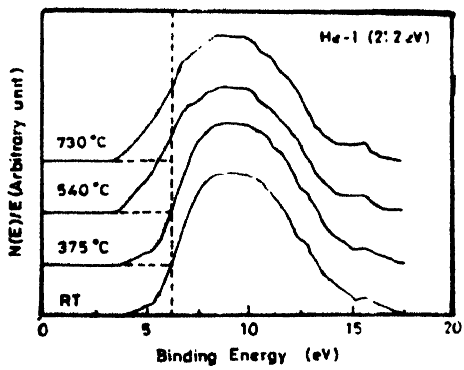

Figure 4. UPS spectra of HF treated n-type silicon (111) surface at different annealing temperature.

the UPS spectra of HF treated silicon surface at different annealing temperatures. Figure 4 shows a typical energy distribution of photo-emitted electrons in the UPS spectra. It can be seen from the figure that after 540°C annealing temperature there is an increase in the counts towards the lower binding energy indicating an increase in the density of surface states close to the valence band.

The present study shows that 5% HF treated silicon surface produces minimum contamination level and unpinning of Fermi level due to surface passivation of silicon dangling bonds by hydrogen and fluorine. Effect of annealing on the HF treated samples upto 540°C shows a shift in the XPS and UPS peak positions towards lower binding energy and beyond this temperature again the pinning of the Fermi level occurs due to desorption of hydrogen from the surface.

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